Synthesis and Characterization of 2- Acetyl Furan Benzoyl Hydrazone and its Applications in the Spectrophotometric Determination of Cu (II)

Abstract

The new chromogenic reagent 2-acetylfuran benzoylhydrazone (AFBH) is synthesised, studied its characteristic properties and applied for the spectrophotometric determination of Copper (II) for the first time. The reagent gives greenish yellow complexes with copper (II) in sodium acetate-acetic acid buffer medium of pH 6.5. The molar absorptivities of copper complex is 2.05 x 104 Lmol-1 cm-1. The colour reactions have been investigated for the micro spectrophotometric determination of copper (II) in aqueous medium and applied for various water and biological samples.

Keywords: Benzoylhydrazone; Spectrophotometric determination; Copper (II); Environment samples

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Introduction

Copper is an important element in biological, industrial and environmental chemistry. Copper plays a key role in biological processes (e.g. Synthesis of haemoglobin, oxidases, enzymes, etc.). It is an important constituent of proteins and enzymes. It is essential for mammals in the synthesis of hemoglobin. Though copper is an essential element, it become hazardous when present in excess. Discharge of copper containing waste into environment leads to the natural imbalance of the ecosystem. Elevated level of copper in soil also affects the growth and metabolism of plants [1]. The excessive accumulation of copper in liver, kidney, brain and cornea [2] leads to failure of liver, mall function of kidney and various neurological abnormalities (Wilson's disease symptoms). For these reasons the analytical monitoring of copper in environmental, biological, industrial, and leafy vegetable and food samples is extremely important. Literature survey indicates that some extractive spectrophotometric method were reported for the determination of copper [3,4].

This paper describes the non-extractive spectrphotometric determination of copper (II) as its AFBH complex in aqueous medium. A close literature survey reveals that AFBH has so far not been employed for the analytical determination of copper (II). This method does not require an extraction step, hence the use of carbon tetrachloride or chloroform as solvent is avoided which are reported as toxic and environmental pollutants and carcinogens. Compare to even some recently published spectrophotometric methods for the determination of copper (II), the present method here offers several distinct advantages.

Experimental

Synthesis of AFBH

2-acetylfuran (2ml, 0.02 mol) in 5ml of methanol, benzoylhydrazide (2.7g, 0.02 mo), dissolved in 10ml of hot water were mixed in a clean round bottom flask. Suitable quantity (~ 2ml) of glacial acetic acid was added to the reaction mixture and refluxed with stirring for 5 hours. Pale yellow coloured product was separated out on cooling. It was collected by filtration, washed several times with hot water and 50 percent cold methanol and recrystalised from ethanol and dried in vacuum yield 2.5 gram, melting point 145-148 ^{0}C (Figure 1).

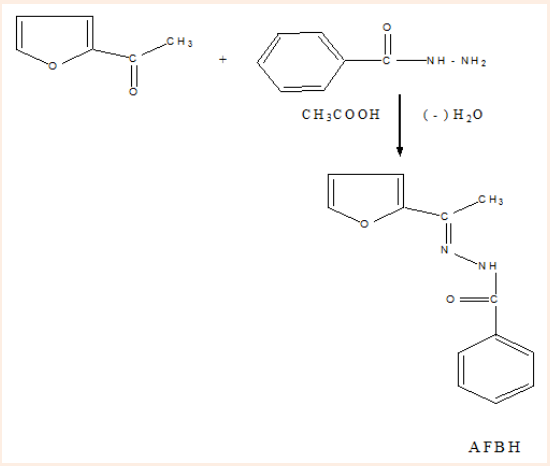

Figure 1: Synthesis of AFBH.

Characterization of AFBH [5]

The compound was chararacterized by IR, NMR, Mass and UV spectral analysis.

i. **Infrared spectrum of AFBH:** shows strong bands at 3228(s), 3117(m), 3031(m), 2950(m), 1653(s), 1605(m), 1590 (s), 1571(m), 1526(s), 1483(m), 1280(s), cm^{-1}

respectively corresponding to υ(NH) secondary, υ (C-H) aromatic stretch(phenyl), υ(C-H) aromatic stretch(Furanyl), υ(C-H) aliphatic stretching, υ(C=O) hydrazine, υ(C=N) azomethine, υ(C-C) aromatic ring, υ(C-C) aromatic ring, υ(C-C) aromatic ring, υ(C-N) stretch vibrations respectively.

ii. **1H-NMR spectrum of AFBH:** (CDCl3 +DMSO-d6) showed signals at 2.33(3H, s), 6.61-7.58 (3H, m) and 7.61-8.6(5H, m) and 10.70 (1H, s) due to CH3, furan and Benzene protons, -NH (imino) groups of hydrazone respectively.

iii. **Mass spectrum of AFBH:** shows molecular ion peak is observed at m/z value of 251. This corresponds to molecular ion peak. It is [M + Na] peak and most intense peak. Another peak is observed at m/z value of 237. It corresponds to M -CH_3 (M minus CH_3).

iv. **The pKa values of AFBH:** The pKa values of AFBH were determined by recording the UV-Visible spectra of micro molar (4 x 10-6 M) solution of the reagent at various pH values and by taking the arithmetic means of the values obtained from the measurements at different wavelengths determined spectrophotometrically using Phillip and Merritt method. The values of deprotonation of AFBH are 5.93 (pK1) and 8.66 (pK2) corresponding to the formation of enol form and conjugated mono anion form respectively.

v. The compound shows strong absorption band in UV region due to π -π* transition. In alkaline medium (pH 8.0-10.0), this band is shifted towards higher wavelength due to formation of conjugated negative anion. The chromogenic characteristics of AFBH are given in Table 1.

Table 1: Chromogenic characteristics of AFBH.

Metal ion	λ_{max}	ε l.mol^{-1}cm^{-1}	pH range	Colour of the Complex
Cu(II)	360	2.06 x 10^4	6.5	Pale greenish yellow
Hg(II)	363	2.5 x 10^3	6.5	Greenish yellow
Fe(III)	360	1.4 x 10^3	6.0	Deep yellow with red tingle
Cr(III)	363	3.2 x 10^3	6.0	Deep yellow
Pb(II)	380	5 x 10^4	6.0	Yellowish
Ni(II)	380	3.9 x 10^3	6.0	Greenish yellow
Cd(II)	415	3.9 x 10^3	6.0	Greenish yellow

0.2M sodium acetate -0.2M acetic acid (pH 6.5) was used in the present study. The standard Cu (II), solution (1 x 10^{-2}M) was prepared by using analytical reagent grade Cu $(CH_3COO)_2$ H_2O. The stock solution of copper (II) was standardized using titrimetric and gravimetric methods respectively. Shimadzu 160A UV visible spectrophotometer equipped with 1.0 cm quartz cells and Elico Model LI-120 pH meter were used in present study.

The reactions of some important metal ions were tested at different pH values. The samples were prepared in 25-ml volumetric flask by mixing 10ml buffer, 1ml of metal ion and 1.5ml of 0.001M AFBH solution. The reaction mixture was diluted to mark with distilled water. The absorbance was measured in 350-600 nm range against the reagent blank.

An aliquot of metal ion in the Beer's law validity range 1.02 -10.2 µg/ml of Cu(II) ,10ml of buffer solution (pH 6.5) 2.5ml of DMF and 1.5ml of 1x10^{-2}M AFBH solution were taken in 25-ml standard flask and diluted to the mark with distilled water. The absorbance of the coloured solution as measured at corresponding wavelength (360) against reagent blank. Calibration graph were prepared. The measured absorbance values were used to compute the amount of copper present in the unknown solution.

Results and Discussion

The reagent 2-acetylfuran benzoylhydrazone is easily prepared under reflux conditions. A 0.001M solution of AFBH is stable for more than 12 hours. In buffer medium (pH 6.5), the ligand presumably exists in enolic form and coordinates the divalent metal ion as mono anion.

Determination of copper (II)

Copper (II) reacts with AFBH in acidic pH (6.5) to give coloured complexes. The colour reaction is instantaneous even at room temperature. The order of addition of reagent, metal ion, buffer, 2.5 ml of DMF. A 10-fold molar excess of the reagent is adequate for full colour development. Addition of excess of reagent has no adverse effect on the absorbance of the complexes.

The system obeys Beer's law in the concentration range 1.02-10.2 µg/ml of copper. The molar absorptivity and Sandell's sensitivity of the methods for Cu(II) is found to be 2.06 x 10^4 Lmol^{-1} cm^{-1} and 3.1x 10^3 µg/cm^2 respectively. The specific absorptivity of the system 0.3245 ml/g^{-1}cm^{-1}. The relative standard deviation for ten replicate analysis of Cu (II) is 0.24 percent. Job's **[6]** and Molar ratio methods gave the composition of Cu (II) complex as 1:

1, (M: L). The stability constants of is calculated by Job's method is found to be 5.97 x 10^6 (Figure 2).

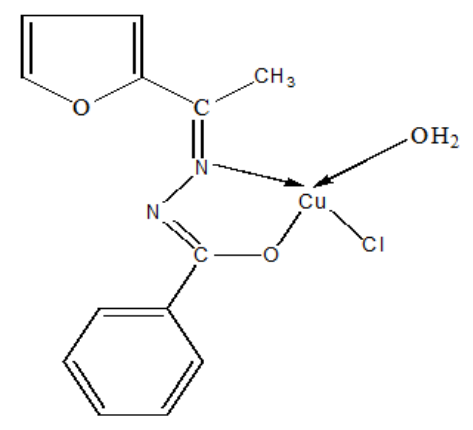

Figure 2: Structure of Cu (II) complex of AFBH [M: L=1:1].

Applications

Determination of copper in green leafy vegetable, soil, biological and samples

The present methods is applied for the determination of Cu(II) in green leafy vegetable, soil and biological samples and results were given (Tables 2 & 3).

Vegetable samples [7-9]: Dry ashing method was used in the analysis of organic samples. A 10 g of dried leafy vegetable sample was taken in a silica dish. The sample was heated over a low burner until the material chars. The charred mass was moistened with 1: 1 HNO_3. Occasionally a 20 percent solution of magnesium nitrate was used for this purpose, particularly if the ash content is very low. Again evaporated to dryness, and transferred to a muffle furnace. The temperature to about 500^0C was reached in the course of about 3 hours. Heating was continued until the ash becomes white. The dish was cooled and the ash was dissolved in a 5 ml portion of 1: 1 HCl. Distilled water was added amounting to about twice the volume of acid added. The solution was filtered to remove any insoluble residue and washed with 1: 4 HCl. The solution was diluted to 50 ml in a standard flask. Aliquots of this sample were taken for the determination of copper by following procedure given above. The results were given in Table 2.

Biological samples [10,11]: A 2-5 g of dried fish and sheep liver samples were taken in a 250 ml beaker. A 6 ml of concentrated nitric acid was added and gently heated for half-an-hour. After the disappearance of the froth, 6 ml of 1: 1 nitric acid and perchloric acid were added. The contents were digested for one hour and repeatedly treated with 6 ml portions of nitric acid and perchloric acid mixture until the solution becomes colourless. The acid solution was evaporated to dryness and the resulting white residue was dissolved in minimum volume of 1M nitric acid and made up to the volume in a 50-ml volumetric flask. Aliquots of this solution were taken for analysis by following recommended procedure given above. The results were given in Table 3.

Table 2: Determination of copper in some leafy vegetable samples.

Name of the Samples[b]	Amount of Copper[a] found (µg/l in Dried Leaves)	
	AFBH Method	Dithizone Method
Thotakura (*Amaranthus gangeticus*)	0.261	0.265
Chukkaku (Irumex vesicarius)	0.261	0.236
Tutikura (*Ipomoea reptuns*)	0.305	0.290
Cauliflower Green (*Brassica deraceavar botntis*)	0.279	0.273
Medicinal Leaves		
Vepaku (*Azadirachta indica*)	0.291	0.275
Gaddi Chamanti (*Tridax procombens L*)	0.123	0.121

a. Average of three determinations.

b. Samples collected from Itikala palli, near SK University, Anantapur

Table 3: Analysis of liver samples.

Liver Sample[b]	Amount of Copper[a] found (µg/ml in Dried Liver)	
	AFBH Method	Dithizone Method
Fish liver	1.289	1.203
Sheep liver	1.258	1.280
Soil Samples[c]		
Urban soil	8.45	8.98
Agricultural soil	7.45	7.41
Road side soil	9.68	9.62

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Range of Copper as per CWI and WWI sites[10]		
	Clean Water	Waste Water
Water	0.003	0.056
Soil	8.39	21.33
Caulioflower	0.391	0.597
Amaranthus	0.221	0.344

a. Average of three determinations.

b. samples collected from Parnapalli Project, Anantapur

c. Anantapur Urban and town area.

Recommended Procedure

A known aliquot of the sample solution was taken in a 25 ml standard flask containing buffer solution of pH 6.5, and reagent [AFBH; 1.5ml 1 x 10^{-2}M; Stock solutions] solution and made up to the mark with distilled water. Absorbance of the solution was measured at λ_{max} against the reagent blank. The absorbance values were referred to the predetermined calibration plot to compute the amount of copper.

a) Soils samples [10-12]

A 2g weight of soil, 5-7 ml of concentrated H_2SO_4 and an excess of $KMnO_4$ are mixed in a conical flask equipped with a reflux condenser. The crystals of $KMnO_4$ are added slowly in small portions, while stirring. It is heated until vapours of SO_3 are evolved. After cooling down, 10 ml of distilled water are added. The excess of $KMnO_4$ and manganese oxides are eliminated by adding H_2O_2. Iron is isolated by precipitation as hydroxide. After filtration, the solution is transferred into 25-ml standard flask and the volume is brought to the mark with distilled water. Aliquots of this solution were taken for analysis by following procedure given above. The results were given in Table 3.

Conclusion

The present was applied to various green leafy vegetables, soil and biological samples and compared with standard Dithizone method [13]. The results were quite encouraging and brings awareness among the public regarding the importance of copper and its adverse effects if present in excess [14].

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